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Removal of styrene using dielectric barrier discharge plasmas combined with sol–gel prepared TiO_2 coated γ-Al_2O_3

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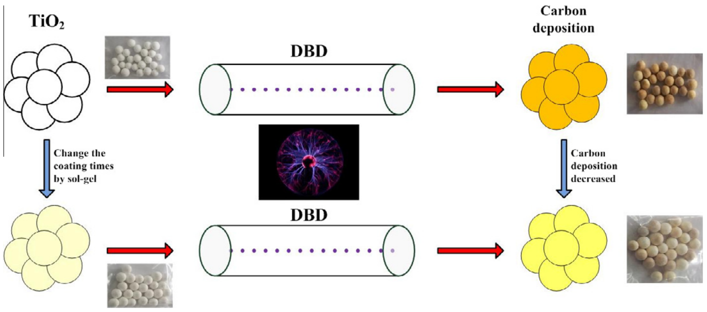
HIGHLIGHTS

- TiO_2 coated γ-Al_2O_3 prepared by sol–gel method was filled in a DBD reactor.
- Compared with P25 coating, loading quantity could be controlled by coating times.
- Styrene removal efficiency and the selectivity of CO and CO_2 were improved.
- The carbon deposition was greatly reduced with increasing of TiO_2 loading quantity.
- The reaction conditions were optimized and reaction mechanism was discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO_2 coated γ-Al_2O_3 prepared by sol–gel method (SG/γ-Al_2O_3) were filled in a dielectric barrier discharge (DBD) reactor to remove styrene which is a typical VOC with high toxicity and odorous smell. Compared with traditional commercial P25 TiO_2 powder coated γ-Al_2O_3 (P25/γ-Al_2O_3), TiO_2 loading quantity could be controlled with different coating times by sol–gel method. However for P25/γ-Al_2O_3, the loading quantity was difficult to be increased because P25 would easily fall off when the coating film got thicker. The calcination temperature and coating times were optimized in this research. The results showed that the SG/γ-Al_2O_3 calcined at 550 °C owned the best catalytic activity and the carbon deposition on catalyst surface could be efficiently reduced with increase of TiO_2 loading quantity, while large amount of carbon deposition was observed on P25/γ-Al_2O_3. Meanwhile O_3 decrease efficiency also improved from 18% with P25/γ-Al_2O_3 to 36% with SG/γ-Al_2O_3 and less O_3 was detected in outlet gas. Other factors like specific input energy (SIE) and oxygen content were also investigated and optimized. When the applied voltage was 12.5 kV, 100% O_2 flowed, the selectivity of CO and CO_2 could reach 100% and nearly no carbon deposition could be observed on TiO_2 surface. Additionally, the formation of by-products, including NO_x, in the reaction system and the plausible reaction mechanism of DBD combined with TiO_2 catalyst were also detected and discussed.

1. Introduction

Volatile organic compounds (VOCs) are primary pollutants in atmosphere and most of them are odor pollutants. Due to their harmful health effects and environmental consequence, how to effectively remove VOC_S becomes a research focus in the field of air pollution control. Many techniques have been successfully developed, for example, carbon adsorption [1], catalytic oxidation [2], biological treatment [3], among which dielectric barrier discharge (DBD) technology has been considered as a promising control technology to reduce VOC_S [4]. However, the single DBD

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technology can hardly mineralize the pollutants completely and leads to potential harmful by-products [5]. Some ordinary transition metals and their oxides, like MnO_2, NiO, CoO and TiO_2 [6–9], are always employed as catalysts to combine with DBD to improve VOC_S removal and mineralization efficiency. TiO_2 as a typical transition metal oxide catalyst has been widely used in the field of environmental pollution control [10,11]. Many researchers found that use of TiO_2 located within the plasma zone had improved the efficiency in VOC_S removal and mineralization [12–17] and a synergy effect had been observed when DBD and TiO_2 were combined in one reactor [18].

Though there are many ways to prepare TiO_2 on a substrate in waste water treatment, such as anodization [19], hydro-thermal synthesis [20], P25 coating [21], chemical vapor deposition (CVD) [22] and sol–gel [10], the TiO_2 can only be coated on a metal substrate by anodization and it is not adapted in DBD reactor, hydro-thermal and CVD need high cost and the synthesis process are complicated, only the P25 coating and sol–gel which have been often used in water treatment are inexpensive and simple methods. In air purification, most researchers used commercial P25 TiO_2 powder coated catalyst combined with DBD plasmas [14,16,23,24]. The removal and mineralization efficiency had been improved by the combination of DBD and P25, however the residual ozone was unsatisfied and carbon deposition on TiO_2 surface was still serious [12,16]. Carbon deposition is always occurred in chemical industry and it can reduce the catalytic activity of the catalyst and reduce the catalyst lifetime. To increase the quantity of catalyst may enhance the catalytic activity to some extent and may reduce the carbon deposition on catalyst surface, however for P25, it is difficult to increase TiO_2 quantity on substrate surface because it will easily fall off when the coating film gets thicker.

The characteristic of sol–gel is that TiO_2 is first deposited in low temperature and then calcined in high temperature. We found that the sol–gel method could overcome the problem above by controlling the coating times to increase TiO_2 loading quantity on γ-Al_2O_3. In this work, the γ-Al_2O_3 coated with different quantity of TiO_2 were filled in a DBD reactor to remove styrene, which was a typical VOCs with odor smell and the results were compared with that obtained with commercial P25 coated γ-Al_2O_3. The carbon deposition and residual ozone were greatly decreased with the increase of TiO_2 quantity on γ-Al_2O_3 surface and other factors like specific input energy (SIE), applied voltage, oxygen content, and the length of discharge region were also investigated and optimized. Additionally, the formation of by-products, including NO_x, in the reaction system and the plausible reaction mechanism of DBD combined with TiO_2 catalyst were also detected and discussed.

2. Experimental

2.1. Experimental setup

The schematic diagram of the experimental system is illustrated in Fig. 1. A wire-tube dielectric barrier discharge (DBD) reactor was used in this work. A total of 0.5 L min^{-1} air flow containing 1000 mg m^{-3} styrene was fed into the reactor. Air flow was regulated by mass flow controllers (S2000, Beijing Sevenstar Electronics Co., Ltd.). The styrene concentration was measured with a gas chromatograph (GC-2010, Shimadzu) equipped with a FID detector and an Rtx-1 column (30 m, 0.32 mm ID, 0.25 pm methylsilicone coating). The removal efficiency of styrene was defined as:

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$

where C_0 and C were the inlet and the outlet concentration of styrene. The NO_x and O_3 were measured by a flue gas analyzer (KM900, Kane International Co. Ltd.) and iodometry method, respectively. The oil like by-products were dissolved by acetone and further detected by gas chromatography and mass spectrometry (GCMS-QP2010, Shimadzu). The gas by-products were also detected by gas chromatography and mass spectrometry. The final products CO_2 and CO were simultaneously measured using a gas chromatograph (GC-14B, Shimadzu) equipped with a FID detector with methane conversion oven. The selectivity to CO and CO_2 are defined as [25]:

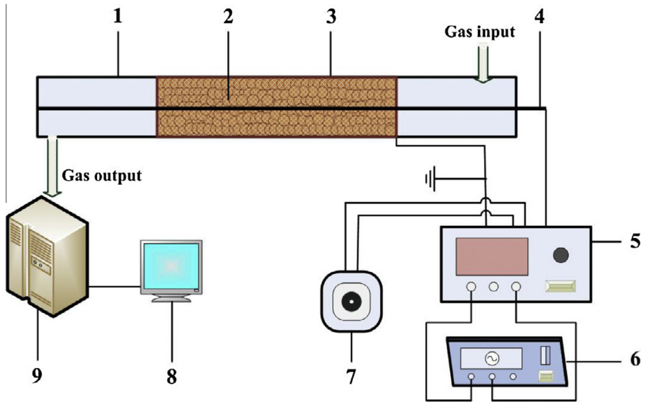

Fig. 1. Schematic of the experimental system setup (1) quartz tube; (2) packing; (3) ground electrode; (4) high voltage electrode; (5) AC power supply; (6) oscilloscope buffer; (7) contact voltage regulator; (8) analytical system; (9) detecting system.

$$S_{CO} = \frac{[CO]}{[C_T]} \times 100\%$$

$$S_{CO_2} = \frac{[CO_2]}{[C_T]} \times 100\%$$

where [CO] and $[CO_2]$ are the amount of CO and CO_2 (mol) after the reaction, $[C_T]$ is the amount of carbon atom (mol) in styrene oxidized during the reaction, which can be calculated by the following equation:

$$[C_T] = ([C_8H_8]_0 - [C_8H_8]) \times 8$$

where $[C_8H_8]_0$ and $[C_8H_8]$ are the amount of styrene (mol) in the gaseous streams before and after the reaction. The background gas was air by purification with active carbon in all the experiment except Section 3.4. The gas composition of Section 3.4 were N_2 (99.9%) and O_2 (99.9%) from cylinder gas. All of the feed gas had 50–55% relative humidity (RH) which detected by hygrometer (AR847, Smart Sensor).

2.2. Plasma reactor and discharge characterization

A wire-tube DBD reactor was used for the present work with a tungsten wire (1.5 mm diameter) as inner electrode, a cylindrical quartz glass tube (35 mm diameter, 1.5 mm thickness) as the dielectric and a thick copper wire mesh wrapping outside the quartz glass tube as an outer electrode (ground electrode). The discharge length was 1.8 cm in this study except optimization experiment of discharge length. In the optimization of discharge length, with the increase of the discharge length, the discharge region and the catalyst amount filled in the reactor also increased, the details of the discharge region and the catalyst amount are listed in Table S1.

The range of applied voltage (RMS) was from 3.6 kV to 16 kV with 10 kHz by an AC power (CTP-2000K, Nanjing Moersi Electronics, China). Removal efficiency, selectivity, NO_x and O_3